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PREPARATION OF OXIRANE (α-EPOXY) COMPOUNDS AND α-GLYCOLS BY OXIDATION OF OLEFINIC COMPOUNDS WITH ORGANIC PERACIDS

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The literature on the preparation of oxirane compounds and α-glycols by oxidation of olefinic compounds with organic peracids is reviewed. Typical experimental procedures for the preparation of organic peracids and their utilization in the preparation of oxirane compounds and α-glycols are given in detail. Approximately three hundred literature references are included.

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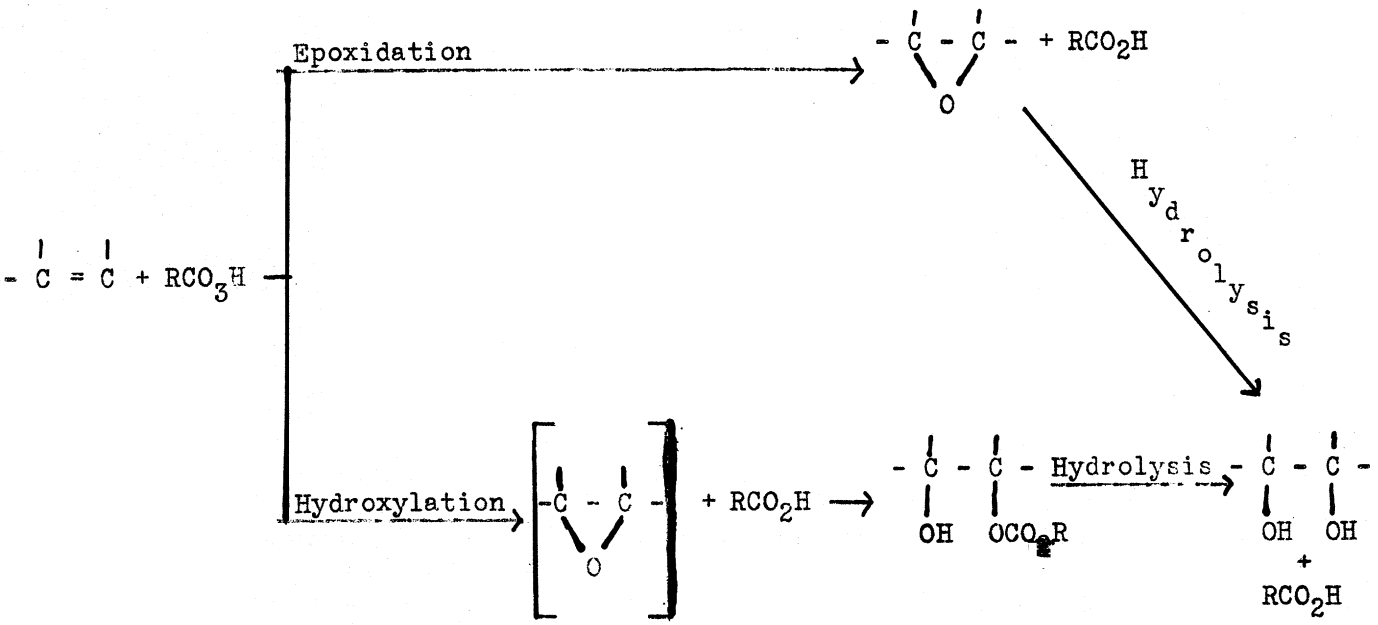
INTRODUCTION

Oxirane (α-epoxy) compounds and α-glycols can be prepared from olefinic compounds by a wide variety of methods. One of the most important and most generally applicable of these, and one which has had its greatest development in recent years, consists in the oxidation of olefinic compounds with organic peracids, as exemplified by the accompanying equations.



Depending upon the peracid employed and/or the operating conditions, either oxirane compounds [217,506,508] or α-glycols [505,506] can be obtained in good yield. Furthermore, the oxirane compounds isolated can, in general, be efficiently converted to the α-glycol.[502] It is important to note that the oxidation step both in epoxidation and hydroxylation reactions with organic peracids is the same, namely, the conversion of the olefinic compound to the oxirane compound, and any attempt to discuss the reactions separately would result in considerable repetition and overlapping. In this chapter, the epoxidation and hydroxylation of olefinic compounds with organic peracids ~~will be~~ are described; ~~and~~ none of the other techniques employed in the preparation of oxirane compounds and α-glycols ~~will be~~ are discussed.

SCOPE

Epoxidation. The discovery that oxirane (α-epoxy) compounds can be prepared from olefinic compounds by epoxidation with an organic peracid is generally credited to the Russian chemist, Prileschajew.[425,428,429,430,431] This investigator showed that perbenzoic acid is an efficient oxidizing agent for this reaction and that the reaction is a general one for the epoxidation of isolated double bonds.

$$-\overset{|}{C}=\overset{|}{C}- + C_6H_5CO_3H \xrightarrow[\text{solvents}]{\text{organic}} -\overset{|}{C}-\overset{|}{C}- + C_6H_5CO_2H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

This epoxidation reaction, which is an excellent one for preparative purposes, proceeds under mild reaction conditions, and it is generally conducted in a non-reactive organic solvent, such as chloroform, ether, benzene, acetone and dioxane. The reaction time is usually short but varies with the number and nature of the groups attached to the ethylenic system.[501] In many of the epoxidation reactions, quantitative or nearly quantitative yields of oxirane compounds are obtained, and as a rule the high yields are the usual experience.

Most investigators have preferred to prepare a solution of perbenzoic acid by any one of the well-known preparative techniques[30,31,138,153,258,303,317,508; 513,564] and have then used this solution for epoxidation purposes. However, since perbenzoic acid can be conveniently and readily prepared by the oxygen oxidation of benzaldehyde,[279,280,281,508,542] some investigators have treated solutions of benzaldehyde and the unsaturated compound with air or oxygen. The perbenzoic acid is consumed as it is formed. This application of the perbenzoic acid epoxidation technique, in which separate preparation and isolation of the peracid is avoided, has been applied to the oxidation of octenes,[407] oleic acid,[447,508] stilbene,[447] styrene,[447] and squalene,[447] and in general good yields of oxirane compounds are obtained.

Epoxidation with perbenzoic acid has been employed in the preparation of oxirane compounds from an extremely large number and wide variety of unsaturated substances, which are listed alphabetically in Table I.

Monoperphthalic acid has also been employed in the preparation of oxirane compounds, but this reagent, although an efficient one, has not been studied so extensively as perbenzoic acid, primarily because it offers little advantage in most reactions. When the epoxidation reaction requires a long period of time for completion, however, the greater stability of monoperphthalic acid, [33,167] compared with that of perbenzoic acid, causes less oxidizing agent to be lost by decomposition. Although Böhme [122,124] was apparently the first to demonstrate that monoperphthalic acid is consumed by reaction with the ethylenic linkage, Chakravorty and Levin [167] were the first investigators actually to isolate oxirane compounds by the oxidation of unsaturated compounds with this oxidizing agent. The epoxidation reaction is conducted under the same conditions as that with perbenzoic acid, and good yields of oxirane compounds are also obtained. Epoxidation with monoperphthalic acid has been applied most extensively to naturally occurring products, such as sterols and polyenes.

Unsaturated substances which have been converted to oxirane compounds by epoxidation with monoperphthalic acid are listed alphabetically in Table II.

Since peracetic acid is one of the most convenient organic peracids to prepare, a study of its possible use as an epoxidizing agent was to be expected. For a long time, however, it was assumed that oxirane compounds could not be prepared by the epoxidation of olefinic compounds with peracetic acid, since the products isolated from such reactions were either α-glycols or hydroxyacetates. The first successful epoxidation with peracetic acid was reported by Böeseken, Smit and Gaster, [111,486] who obtained methyl 9, 10, 12, 13-diepoxystearate from methyl

linoleate, but the yields are extremely poor, the major proportion of the product consisting of a polymer of undetermined constitution.[503] In a systematic study of the reaction of peracetic acid in acetic acid solution and of peracetic acid in an inert solvent with various unsaturated compounds, Arbusow and Michailow [22,23] observed that with the former oxidizing solution they obtained hydroxyacetates, whereas with the latter they obtained good yields of oxirane compounds. They concluded that the behavior of peracetic acid toward olefins is the same as that of perbenzoic acid, namely, conversion of the ethylenic linkage to the oxirane group, but when an acetic acid solution is employed, the oxirane group is converted to the hydroxyacetate by further reaction with acetic acid. The apparent necessity for employing peracetic acid in an inert solvent to obtain good yields of oxirane compounds was a serious drawback to the general applicability of peracetic acid for epoxidation, since peracetic acid can be prepared and used most conveniently in acetic acid, whereas its isolation free (or substantially free) of acetic acid is time-consuming and hazardous.

Subsequently, however, in connection with a kinetic study of the reaction of peracetic acid in acetic acid solution with various long-chain olefinic compounds, Findley, Swern and Scanlan [217] defined suitable reaction conditions for the efficient conversion of olefinic compounds to oxirane compounds. These investigators pointed out that in order to obtain good yields of oxirane compounds it was necessary to operate at moderate temperatures (20 to 25° was preferred), the reaction time should be as short as possible and strong acids, which catalyze the opening of the oxirane ring by acetic acid, must not be present in the reaction mixture. The reaction was shown to be a general, and afforded a simple and convenient method for the preparation of large quantities of oxirane compounds. Isolation of pure peracid and employment of inert solvents were unnecessary. Yields of

oxirane compounds, however, were usually lower than when perbenzoic or monoperphthalic acid was employed.

Unsaturated substances which have been converted to oxirane compounds by epoxidation with peracetic acid are listed alphabetically in Table III.

Percamphoric acid has been employed to convert d-pinene and cholesterol to the corresponding oxirane compounds;[357] but no other examples of epoxidation with this peracid could be found. α-Diisobutylene is the only olefin which has been reported to yield an isolable oxirane compound on epoxidation with performic acid.[159c] Furthermore, the diisobutylenes behave abnormally on reaction with performic and peracetic acids, yielding, besides the expected products, unsaturated alcohols, an aldehyde, a ketone, a cyclic diether and high-boiling products.[159b, 159c, 160, 259a, 260]

Hydroxylation. Use of peracetic acid for the preparation of α-glycols from unsaturated substances probably exceeds that of all other organic peracids combined. Peracetic acid is usually prepared and employed in two ways: (1) the peracid is preformed by the reaction of acetic acid or acetic anhydride with 25 to 90% hydrogen peroxide[91,97,182,184,185,189,205,217,233,236,479,480,486] and then mixed with the unsaturated compound, or (2) the unsaturated compound is mixed with hydrogen peroxide and acetic acid and the peracetic acid is consumed as it is formed.[24, 46,70a,120,196,199,231,232,235,262,263,264,265,267,269,270,271,272,297,351,395, 406, 412,463,483,491,492,505,509] Under certain conditions oxirane compounds can be obtained in good yields, as discussed earlier,[217] but as the reactions have usually been carried out (long reaction times and/or high temperatures, and/or sulfuric acid present), the products isolated are hydroxyacetates, obtained by the reaction of excess acetic acid with the oxirane compound formed initially. These are readily hydrolyzable to the α-glycol in excellent yield.[262,264,479,480] Although good yields of glycols were reported by some early investigators, the operating conditions employed caused the loss of much active oxygen by decomposition. By the use of sulfuric acid as the catalyst and by employing moderate temperatures (40°) and short reaction periods, Swern and co-workers[505] obtained excellent yields of α-glycol with stoichiometric quantities of 25 to 30% hydrogen peroxide. Since

the acid catalyzes the formation of peracetic acid and since the peracid is rapidly consumed at 40°, the reaction is complete in a few hours, and little active oxygen is lost. This procedure is one of the most efficient for converting long-chain olefinic compounds to α-glycols. Slightly higher yields of α-glycols were reported by Greenspan,[232] who employed 90% hydrogen peroxide instead of the less concentrated grade.

Unsaturated substances which have been converted to α-glycols by oxidation with peracetic acid, either preformed or prepared and utilized "in situ", are listed alphabetically in Table IV. Some of the unsaturated substances listed have been converted to hydroxyacetates rather than to α-glycols, but the conversion to glycol is effected so readily by hydrolysis that these substances have also been included.

An even more efficient and more rapid hydroxylation technique than that just discussed was first described by Swern and co-workers,[505] it consists in the reaction of unsaturated compounds with performic acid. Not only does performic acid display an unexpectedly high rate of formation when 25 to 90% hydrogen peroxide and formic acid are mixed,[182,184,185,189,233,507,525] but it also reacts rapidly and completely with the unsaturated linkage. By means of this hydroxylation reaction, almost quantitative conversion of the unsaturated compound to α-glycol is accomplished within a short time, and approximately stoichiometric quantities of hydrogen peroxide can be employed. The initial product of oxidation is not the α-glycol, however, but the oxirane compound, which is rapidly converted to hydroxyformates as a result of the high acidity of formic acid. The hydroxyformates are the products isolated, and these are readily converted to the α-glycol by hydrolysis with dilute aqueous alkali or even by exposure to moist air or heating with water.[502] It is important to note that performic acid is preferably not prepared separately because of its instability, with resulting

loss of active oxygen,[189,233,507,525] but it is prepared and utilized "in situ".[505] Somewhat more complete hydroxylation is obtained by employing 90% hydrogen peroxide instead of the 25 to 30% concentration.[232]

English and Gregory[204] showed that concentrated solutions of performic acid can be used in the hydroxylation of α,β-unsaturated acids giving fair yields of the dihydroxy acids within a relatively short time. Earlier workers who had employed dilute solutions of organic peracids had either been unable to hydroxylate such compounds or used extremely long reaction times, with concomitant loss of active oxygen.

Unsaturated substances converted to α-glycols by oxidation with performic acid are listed alphabetically in Table V.

Ordinarily, perbenzoic, monoperphthalic and percamphoric acids are not considered hydroxylating reagents, since the products obtained in the oxidation of unsaturated substances with these oxidizing agents are usually the oxirane compounds. Since, in most cases, oxirane compounds can be converted to α-glycols in quantitative yield, these peracids can be employed for the preparation of α-glycols, and in some cases this series of reactions has been carried out. In general, there is no advantage in employing the aromatic peracids to prepare α-glycols when two more efficient peracids are available for this purpose, namely, performic and peracetic acids, either preformed or prepared and used "in situ". Under some reaction conditions, however, perbenzoic acid has converted the ethylenic linkage either to the α-glycol group or to a benzoate ester readily hydrolyzable to the α-glycol, and oxirane compounds are not isolated. In these cases water has been present or reaction times have been exceptionally long.

Unsaturated substances which have been converted to α-glycols or to hydroxybenzoates by oxidation with perbenzoic acid are listed in Table VI.

SELECTION OF EXPERIMENTAL CONDITIONS

Since the oxirane group is extremely reactive, and undergoes ring opening reactions with various types of compounds which contain active hydrogen atoms, it is obvious that conditions for epoxidation reactions must be selected with care. Of paramount importance in obtaining high yields of oxirane compounds is the avoidance of strongly acidic materials in the reaction mixture[505] and high reaction temperatures.[217] In epoxidations with perbenzoic and monoperphthalic acids an inert solvent is employed; in epoxidation with peracetic acid, acetic acid may be used as the solvent provided that strong acids are absent and low reaction temperatures are employed (30° or lower).

With unsaturated substances containing isolated double bonds, the epoxidation reaction is rapid and complete, usually within eight to twenty-four hours at room temperature or below. If electron-releasing groups are attached to or are in close proximity to the ethylenic linkage, the reaction is considerably accelerated;[501] if electron-attracting groups are attached to or are in close proximity to the ethylenic linkage, the reaction is slowed down.[501] In Table VII the specific reaction rates (k) are given for the reaction of aliphatic and alicyclic olefins with peracetic acid in acetic acid solution; in Table VIII are given the specific reaction rates for the reaction of aliphatic and alicyclic olefins with perbenzoic acid; and in Table IX are given the specific reaction rates for the reaction of olefins containing aromatic groups with peracetic acid in acetic acid solution and with perbenzoic acid in chloroform or carbon tetrachloride solution. The wide range of specific reaction rates in related groups of compounds is shown most strikingly by comparing ethylene with 2-methyl-2-butene (Table VII), cyclobutene with 1-methylcyclopentene (Table VII), sorbic acid with oleic acid (Table VIII), allylbenzene with 1-phenyl-1-propene (Table IX),

1,4-dihydronaphthalene with 1,2-dihydronaphthalene (Table IX), cinnamic acid with cinnamyl alcohol (Table IX), 1-phenyl-2-butene with 1-phenyl-1-butene (Table IX), eugenol with isoeugenol (Table IX), and safrole with isosafrole (Table IX). Furthermore, the specific reaction rate of tetramethylethylene with peracetic acid at 25.8° is too high to be measured.[114,115]

The time variable in these oxidation reactions can be readily determined with a minimum of experimental effort by measuring unconsumed peroxide at suitable time intervals.[138,303,304a,338b,560a] By following the disappearance of active oxygen, the reaction can be terminated at exactly the right time, thereby holding side reactions and loss of active oxygen to a minimum. Furthermore, the determination of unconsumed peroxide should be carried out in all peracid oxidations in which distillation techniques are employed in the recovery of solvent and in the isolation of reaction products. In reactions which proceed slowly, a large amount of unconsumed peracid may be present in the distillation charge and cause an explosion if the peroxide is not destroyed.

Although a wide range of reaction conditions can be employed in the preparation of α-glycols, temperatures above 50° are undesirable if, in addition to obtaining high yields of α-glycol, one also wishes to employ stoichiometric quantities of hydrogen peroxide or peracid, since above this temperature loss of active oxygen becomes significantly high. Early workers, who were not concerned with efficient use of active oxygen, operated at high temperatures and of necessity employed large excesses of hydrogen peroxide or peracid. Furthermore, reaction temperatures below 5-10° may also be disadvantageous since they make the reaction time objectionably long.

To help in the selection of hydroxylation techniques the methods just discussed are listed in decreasing order of efficiency and overall

mildly exothermic soon after the addition of hydrogen peroxide is started, and cooling is then required for three to four hours after the addition is complete to maintain the temperature at 40° (bath temperature 25-30°). The solution is allowed to stand overnight at room temperature. The concentration of peracetic acid is then about 0.8 to 1.2 M (about 6-9%). The yield is 60-90%. The solution contains diacetyl peroxide and some unconverted hydrogen peroxide, in addition to peracetic acid and acetic acid.

A concentrated solution of peracetic acid[233] is prepared by cautiously adding 9.1 g. of 90% hydrogen peroxide to a stirred solution of 10 grams of acetic acid and 0.11 ml. of concentrated sulfuric acid contained in a flask immersed in a water bath at 22-23°. At the end of four hours, the peracetic acid content of the solution is about 44%, and it rises to a maximum of 46% within twelve to fifteen hours.

The peroxidic components in the peracetic acid solutions just described are determined on a single sample as follows[184,185]: 0.2 to 2 ml. of the solution (accurately dispensed from a pipette or weighed) is diluted with 50 ml. of 4N aqueous sulfuric acid which has been cooled to 0°. This solution is rapidly titrated with 0.1 N potassium permanganate to a pink end point. This determines the unreacted hydrogen peroxide. One ml. of 0.1 N potassium permanganate is equivalent to 0.00170 g. of hydrogen peroxide. The peracetic acid is determined by adding 2 ml. of saturated aqueous potassium iodide to the same solution and rapidly titrating with 0.1 N sodium thiosulfate, starch indicator being used. One ml. of 0.1 N sodium thiosulfate is equivalent to 0.00380 g. of peracetic acid. At this point, the flask and its contents are heated on the steam bath for five to ten minutes, causing a return of the blue color, and the liberated iodine is titrated with 0.1 N sodium thiosulfate. The last titration gives the diacetyl peroxide content. One ml. of 0.1 N sodium thiosulfate is equivalent to 0.00590 g. of diacetyl peroxide. Greenspan and MacKellar[233a], however, have recently reported that ceric sulfate is more satisfactory than potassium permanganate for determination of residual hydrogen peroxide.

seven weeks.[233] The 45% solution retains 94% of the peracid after seven weeks storage if it is stabilized with sodium pyrophosphate[233] (other stabilizers have also been suggested[377,451]). Five to 10% solutions of peracetic acid in acetic acid, however, show significant losses of active oxygen at room temperature but little loss at 0 to 5°.[217] Although peracetic acid can be prepared by efficient processes, and only a small amount of active oxygen is lost or unavailable for oxidative purposes, the separate preparation of the peracid is a time-consuming step in the hydroxylation reaction, and method 2 is more desirable. Concentrated solutions of peracetic acid have recently become commercially available.[156]

There is a wide variety of methods for preparing organic peracids, and many solvents have been suggested for use in their preparation, isolation and application as oxidizing agents. This phase of peracid chemistry is not sufficiently pertinent to be discussed in detail, but information has recently been published on this subject.[500a] The particular oxidative method and solvent selected will depend, in large part, on the solubility of the peracid, the unsaturated substance, and the oxidation products. Furthermore, the stability of the peracid and the oxidation products in the solvent medium, as well as the ease of separation of the desired products from the other materials present has an important bearing on the reaction conditions selected. The solvent has been reported to have an effect on the rate of decomposition of peracids as well as on their rate of reactions with unsaturated substances.[47,89,161,303,311,346,429]

For information regarding other organic peracids (properties, methods of preparation, etc.), the recent review article by Swern[500a] should be consulted. Furthermore, special techniques for preparing organic peracids, which may be advantageous for some types of work, are described in that article.

of perbenzoic acid remains. The benzoic acid is removed from the chloroform solution by shaking with several portions of 10% sodium hydroxide solution, the alkali is removed by washing with water, and the chloroform solution is dried over anhydrous sodium sulfate. Fractional distillation yields 24-26 g. of 1,2-epoxyethylbenzene, b.p. 101°/40 mm., as an almost colorless liquid. The yield is 69-75% of the theoretical amount.

9,10-Epoxystearic Acid.[503,508] To 750 ml. of an acetone solution of perbenzoic acid, prepared as described earlier,[508] containing 0.4 mole of perbenzoic acid, 85 g. (0.3 mole) of oleic acid[154a,508a,560b] is added at 0-5°. After standing for forty hours at room temperature, the solution is cooled to -25° and filtered, and the precipitate is washed once with cold acetone. The crude 9,10-epoxystearic acid (purity 95-99%) is a white powder weighing about 85 g. Two recrystallizations from acetone at 0 to -25° yields 55-60 g. of analytically pure 9,10-epoxystearic acid, m.p. 59.5-59.8°. Oxirane oxygen:[507a] calcd., 5.36%; found, 5.33-5.37%. The yield is 62-67%.

1,2-Epoxy-2-Methyl-3-Butene (Isoprene Monoxide) (Preferential Oxidation).[438] To a stirred solution of 16 g. (0.235 mole) of isoprene in 50 ml. of ethyl chloride cooled in an ice bath, a cold solution of 30 g. (0.217 mole) of perbenzoic acid in 150 ml. of ethyl chloride is added from a dropping funnel. The reaction flask and dropping funnel are protected from the atmosphere by drying tubes. After the perbenzoic acid solution has been added, the reaction flask is allowed to stand in the refrigerator until the oxidizing agent is completely consumed (approximately twenty-four hours). The solution is then cautiously shaken with double the calculated quantity of sodium bicarbonate solution (30 g. per 100 ml. of water) in a cooled separatory funnel until evolution of carbon dioxide ceases. The aqueous layer is discarded, and the ethyl chloride solution is dried overnight in the

is swirled vigorously and continuously during the addition. There is no need to wait four to five minutes, as specified by Braun,[138] before extracting the mixture with water.

(b) Instead of transferring the chloroform-methanol solution containing sodium perbenzoate to a separatory funnel, about 150 ml. of water containing chopped ice is added to the reaction mixture, which is being rapidly swirled. The mixture is then transferred to the separatory funnel, and 350 ml. of water containing chopped ice is added to the rapidly swirled material. In this way, the formation of lumps, which dissolve slowly, is prevented.

(c) The emulsion that collects at the interface of the aqueous sodium perbenzoate phase and the chloroform phase is discarded. Only three to five minutes is allowed for separation of the phases. Likewise, emulsions formed during the washing of the aqueous layer are discarded.

(d) The aqueous phase is washed with two 100 ml. portions of carbon tetrachloride, instead of ~~with~~ chloroform.

(e) After acidification, the aqueous solution is extracted with reagent grade benzene rather than ~~with~~ chloroform. At this point, the temperature of the solution should be above 5°, to prevent freezing of the benzene.

(f) The benzene solution is washed with water, dried over anhydrous sodium sulfate (calcium chloride sometimes causes a sudden decomposition of the peracid[138]), and stored in the dark at about 10° until used.

Benzene solutions of perbenzoic acid are more stable than those containing chloroform, and Kolthoff's method of preparation is recommended when large quantities of perbenzoic acid solution are made at one time, and must be stored. Crystalline perbenzoic acid can be obtained by removal of the solvent under vacuum, as described in Organic Syntheses,[138] and purified by recrystallization from chloroform-ethanol

mixtures[335] or from petroleum ether.[31] It melts at about 41° and is soluble in the common organic solvents, except cold petroleum ether.

Perbenzoic Acid (Benzaldehyde-Air Method).[508] For the preparation of large laboratory quantities of perbenzoic acid, the air oxidation of benzaldehyde in acetone solution while irradiating it with ultraviolet light is convenient.

In a 5-liter three-neck Pyrex flask equipped with a thermometer, a solid carbon dioxide-cooled reflux condenser, and two fritted glass discs placed back-to-back through a tightly fitting cork in the center neck, 520 g. (4.9 moles) of freshly distilled benzaldehyde is dissolved in 4000 ml. of acetone. The flask is immersed in an ice-water bath and irradiated from the top with three 125-watt quartz mercury vapor lamps, symmetrically placed around the flask, while a rapid stream of dry air is passed through the fritted discs and into the solution for twenty-four hours at 5-10°. The reaction is conducted in a fume hood because of the formation of ozone. If the reaction cannot be run without interruption, the acetone solution can be stored at 5-10° with little or no loss of perbenzoic acid. After about twenty-four hours, the rate of peracid formation decreases considerably and the solution then contains about 2 moles of perbenzoic acid. The yield is 40-45%.

Perbenzoic acid in an organic solvent can be determined iodometrically by shaking the solution with an aqueous acetic acid solution of potassium iodide: A known volume of the perbenzoic acid solution is pipetted into an iodine flask containing 50 ml. of 0.4 N acetic acid and 1 g. of potassium iodide, the mixture is shaken, and the liberated iodine is titrated with 0.05-0.1 N sodium thiosulfate solution, starch indicator being used. However, in following the course of the oxidation of water-insoluble substances which precipitate upon addition of the solution to the aqueous acetic acid and thereby cause difficulty in obtaining a good end-point, the perbenzoic acid solution is added to 25 ml. of a chloroform-acetic acid solution (3:2 by volume). Two ml. of saturated potassium iodide is

added and the solution is allowed to stand for five minutes. Seventy-five ml. of water is added, the solution is well shaken, and the liberated iodine is titrated with 0.05-0.1 N sodium thiosulfate.[560a] One ml. of 0.1 N sodium thiosulfate is equivalent to 0.00690 g. of perbenzoic acid.

Monoperphthalic Acid. The procedure described in Organic Syntheses,[123] consisting in the reaction of phthalic anhydride with alkaline 30% aqueous hydrogen peroxide is satisfactory, giving 65-70% yields. Bachman and Cooper[25] have reported that it is advantageous to employ 40% sodium hydroxide solution and to add crushed ice directly to the reaction mixture. In this procedure, the peracid is extracted with ether, but if ether is not a suitable solvent for subsequent oxidation reactions, it can be readily removed and replaced by dioxane or other solvent.[123] The separation of the ether is described in Organic Syntheses[123].

Monoperphthalic acid can be determined by the same methods employed for perbenzoic acid. An alternate procedure[123] is to add 2 ml. of the solution to 30 ml. of 20% aqueous potassium iodide and titrate the liberated iodine after ten minutes with 0.05 N sodium thiosulfate solution. One ml. of 0.05 N sodium thiosulfate solution is equivalent to 0.00455 g. of monoperphthalic acid.

Peracetic Acid.[217,233] In a 5-l. three-neck flask equipped with a mechanically driven glass stirrer, a thermometer and a separatory funnel, 2250 g. of acetic anhydride, which has been filtered through glass wool to remove particles which may catalyze peroxide decomposition, is added. The thermometer should not be placed within a thermometer well but should be immersed in the liquid, and at least one neck of the flask should be open to the atmosphere. The acetic anhydride is warmed to 35-40° in a water bath into which cold or warm water can be run at will and rapidly removed if necessary. By means of the separatory funnel, 500 g. of 25-30% hydrogen peroxide is added in about one hour with agitation, the temperature being maintained at 40°. The reaction becomes

mildly exothermic soon after the addition of hydrogen peroxide is started, and cooling is then required for three to four hours after the addition is complete to maintain the temperature at 40° (bath temperature 25-30°). The solution is allowed to stand overnight at room temperature. The concentration of peracetic acid is then about 0.8 to 1.2 M (about 6-9%). The yield is 60-90%. The solution contains diacetyl peroxide and some unconverted hydrogen peroxide, in addition to peracetic acid and acetic acid.

A concentrated solution of peracetic acid[233] is prepared by cautiously adding 9.1 g. of 90% hydrogen peroxide to a stirred solution of 10 grams of acetic acid and 0.11 ml. of concentrated sulfuric acid contained in a flask immersed in a water bath at 22-23°. At the end of four hours, the peracetic acid content of the solution is about 44%, and it rises to a maximum of 46% within twelve to fifteen hours.

The peroxidic components in the peracetic acid solutions just described are determined on a single sample as follows[184,185]: 0.2 to 2 ml. of the solution (accurately dispensed from a pipette or weighed) is diluted with 50 ml. of 4N aqueous sulfuric acid which has been cooled to 0°. This solution is rapidly titrated with 0.1 N potassium permanganate to a pink end point. This determines the unreacted hydrogen peroxide. One ml. of 0.1 N potassium permanganate is equivalent to 0.00170 g. of hydrogen peroxide. The peracetic acid is determined by adding 2 ml. of saturated aqueous potassium iodide to the same solution and rapidly titrating with 0.1 N sodium thiosulfate, starch indicator being used. One ml. of 0.1 N sodium thiosulfate is equivalent to 0.00380 g. of peracetic acid. At this point, the flask and its contents are heated on the steam bath for five to ten minutes, causing a return of the blue color, and the liberated iodine is titrated with 0.1 N sodium thiosulfate. The last titration gives the diacetyl peroxide content. One ml. of 0.1 N sodium thiosulfate is equivalent to 0.00590 g. of diacetyl peroxide. Greenspan and MacKellar[233a], however, have recently reported that ceric sulfate is more satisfactory than potassium permanganate for determination of residual hydrogen peroxide.

In following the consumption of active oxygen during the oxidation of water-insoluble substances with peracetic acid, the procedure described under the preparation of perbenzoic acid should be employed.[560a] This procedure determines total active oxygen and not peracetic acid alone, but the difference between the titrations at succeeding time intervals gives a measure of peracetic acid consumed.

Performic acid.[233,507,525] In a 500 ml. Erlenmeyer flask, 25 g. of 25-30% hydrogen peroxide and 250 g. of 98-100% formic acid are mixed at room temperature. Since the reaction is only mildly exothermic (temperature rise 1-2°), no cooling is required in batches of this size. The maximum content of performic acid (approximately 5%) is obtained within thirty to sixty minutes, as determined by the analytical techniques just described for peracetic acid.

A concentrated solution of performic acid is prepared[204,233] by cautiously adding 28.4 g. of 90% hydrogen peroxide to a stirred solution of 23.0 g. of 98-100% formic acid and 0.28 ml. of concentrated sulfuric acid contained in a flask immersed in a water bath at 22-23°. Maximum performic acid concentration (approximately 35%) is reached within thirty minutes.

Performic acid solutions are unstable, and active oxygen is lost at a fairly rapid rate (several percent per hour at room temperature); the solutions, therefore should not be stored but should be used up immediately.

EPOXIDATION WITH PERBENZOIC ACID

1,2-Epoxyethylbenzene (Styrene Oxide).[258,259] To a solution of 42 g. (0.30 mole) of perbenzoic acid in 500 ml. of chloroform, prepared as described earlier,[138] 30 g. (0.29 mole) of styrene is added. The solution is maintained at 0° for twenty-four hours, with frequent shaking during the first hour. At the end of twenty-four hours, titration of an aliquot part of the solution shows that only the slight excess

of perbenzoic acid remains. The benzoic acid is removed from the chloroform solution by shaking with several portions of 10% sodium hydroxide solution, the alkali is removed by washing with water, and the chloroform solution is dried over anhydrous sodium sulfate. Fractional distillation yields 24-26 g. of 1,2-epoxyethylbenzene, b.p. 101°/40 mm., as an almost colorless liquid. The yield is 69-75% of the theoretical amount.

9,10-Epoxystearic Acid.[503,508] To 750 ml. of an acetone solution of perbenzoic acid, prepared as described earlier,[508] containing 0.4 mole of perbenzoic acid, 85 g. (0.3 mole) of oleic acid[154a,508a,560b] is added at 0-5°. After standing for forty hours at room temperature, the solution is cooled to -25° and filtered, and the precipitate is washed once with cold acetone. The crude 9,10-epoxystearic acid (purity 95-99%) is a white powder weighing about 85 g. Two recrystallizations from acetone at 0 to -25° yields 55-60 g. of analytically pure 9,10-epoxystearic acid, m.p. 59.5-59.8°. Oxirane oxygen:[507a] calcd., 5.36%; found, 5.33-5.37%. The yield is 62-67%.

1,2-Epoxy-2-Methyl-3-Butene (Isoprene Monoxide) (Preferential Oxidation).[438] To a stirred solution of 16 g. (0.235 mole) of isoprene in 50 ml. of ethyl chloride cooled in an ice bath, a cold solution of 30 g. (0.217 mole) of perbenzoic acid in 150 ml. of ethyl chloride is added from a dropping funnel. The reaction flask and dropping funnel are protected from the atmosphere by drying tubes. After the perbenzoic acid solution has been added, the reaction flask is allowed to stand in the refrigerator until the oxidizing agent is completely consumed (approximately twenty-four hours). The solution is then cautiously shaken with double the calculated quantity of sodium bicarbonate solution (30 g. per 100 ml. of water) in a cooled separatory funnel until evolution of carbon dioxide ceases. The aqueous layer is discarded, and the ethyl chloride solution is dried overnight in the

refrigerator with anhydrous sodium sulfate. The solution is filtered and the filtrate is distilled through a Widmer column until unreacted isoprene begins to distill. The residual material is then distilled twice through a spiral-type fractionating column, yielding a fraction boiling at 81°/735 mm. and consisting of pure 1,2-epoxy-2-methyl-3-butene (isoprene oxide). The yield is 30-40%.

EPOXIDATION WITH MONOPERPHTHALIC ACID

β-and α-Cholesteryl Oxide Acetates.[167] Ten grams (0.023 mole) of cholesteryl acetate, m.p. 112-114°, dissolved in 50 ml. of ether, is mixed with 266 ml. of an ether solution containing 8.4 g. (0.046 mole) of monoperphthalic acid. The solution is refluxed for six hours, and the solvent is removed by distillation. The residue is dried under vacuum, and digested with 250 ml. of chloroform which has been dried over anhydrous potassium carbonate. The mixture is filtered, yielding 6.7 g. of phthalic acid (87% recovery) and a colorless solution, from which the solvent is removed under vacuum. The residue is crystallized from 30 ml. of methanol, giving 6.0 g. (58% yield) of *β*-cholesteryl oxide acetate, which on recrystallization gives the pure product, m.p. 111-112°, $[\alpha]_D^{25}$ -21.8°. Concentration of the filtrate gives 1.55 g. (15% yield) of α-cholesteryl oxide acetate. The α-isomer, purified by crystallization from ethanol, has a m.p. of 101-103°, $[\alpha]_D^{25}$ -44.6°.

HYDROXYLATION WITH HYDROGEN PEROXIDE-FORMIC ACID

9,10-Dihydroxystearic Acid, Low Melting Isomer.[505] To a well-stirred solution of 141 g. (0.5 mole) of oleic acid[154a,508a,560b] in 423 ml. of 98-100% formic acid in a 1 l. three-neck flask at 25°, sufficient 30% (100 volume) hydrogen peroxide solution to provide 17.5 g. (0.513 mole; 2.5% excess) of hydrogen peroxide is added over a fifteen minute period. The reaction becomes vigorously exothermic after a time lag of ~~about~~ five to ten minutes, and homogeneous ~~about~~ twenty to thirty minutes after all the hydrogen peroxide has been added. The temperature

is maintained at 40° with a cold water bath at the beginning and ~~with~~ a warm water bath toward the end of the reaction. After about two hours, no further consumption of peroxide is observed, and the formic acid is removed by distillation under reduced pressure (b.p. 50°/125 mm.) in a stream of carbon dioxide or nitrogen to prevent bumping. The residue in the flask, which consists of hydroxyformoxystearic acids, is heated for one hour at 100° with an excess of 3N aqueous sodium hydroxide, and the hot pale yellow soap solution is slowly poured into an excess of 3 N hydrochloric acid with stirring. The oil which separates is allowed to solidify, and the aqueous layer is discarded. The white solid is remelted with hot water on the steam bath, and stirred well to remove residual salts and water-soluble acids. When the oil has resolidified, the aqueous layer is discarded, and the solid is broken into small pieces and air-dried. This product which consists of fairly pure 9,10-dihydroxystearic acid (iodine number, about 2-4; neutralization equivalent, 315-320), weighs about 150-155 g. and melts at about 92°. The yield is 97-99%. The small quantity of unsaturated material present can be readily separated by grinding the material and washing it by decantation with several portions of ~~Skellysolve B, b.p. 65-70°.~~ petroleum naptha, hexane fraction, boiling range 63-70°. From 50 g., 47 g. of 9,10-dihydroxystearic acid, m.p. 93°, and iodine number 0.0, is obtained. To obtain an analytically pure product, the dihydroxystearic acid is recrystallized from 95% ethanol, yielding 9,10-dihydroxystearic acid, m.p. 95°, in 80% overall yield.

If purified oleic acid is not available, red oil (commercial product containing about 60-75% oleic acid) may be employed instead. The crude 9,10-dihydroxystearic acid, however, melts at about 70-75°, as compared with 92° when pure oleic acid is used, and several recrystallizations from alcohol are required to obtain a pure product. The yield of 9,10-dihydroxystearic acid from red oil is about 50-60% of the available oleic acid. Furthermore, the 90% grade

of formic acid is satisfactory, but the reaction mixture remains heterogeneous throughout. In runs one-tenth the size described, the 25-30% hydrogen peroxide can be added in one portion. In larger runs, the addition may require thirty minutes to one hour. In runs five to ten times the size described, it is more convenient to pour the reaction mixture into a large volume of water, and then process the washed oily layer, consisting of hydroxyformates, [redacted] as described.

When 90% hydrogen peroxide is employed instead of the 30% grade, the crude dihydroxystearic acid has an iodine number of 1, instead of 2-4. Furthermore, with the concentrated peroxide, the quantity of formic acid can be reduced to about one-seventh the amount employed with 25-30% hydrogen peroxide.

1,2-Tetradecanediol.[506] To a well-stirred mixture of 49.2 g. (0.25 mole) of 1-tetradecene, b.p. 158-9°/60 mm., nD^{20} 1.4357 (prepared by efficient fractional distillation of the ~~purest~~ 95% commercial grade, ~~obtained from the Connecticut Hard Rubber Co.~~) and 295 ml. of 98-100% formic acid at 25°, 35 g. of 25.6% hydrogen peroxide (0.263 mole; 5% excess) is added in one portion. The mixture is heated and stirred for about twenty-four hours at 40°, or until an analysis[560a] indicates that the theoretical quantity of peroxide has disappeared. The reaction mixture is heterogeneous throughout. The formic acid is recovered under reduced pressure and the distillation residue is refluxed for one hour with excess 3 N alcoholic potassium hydroxide. Most of the alcohol is then evaporated on the steam bath, and a large quantity of hot water is added, precipitating the glycol as an oil. When the glycol has solidified, the water layer is siphoned off, and the product is remelted with hot water and allowed to resolidify. The combined water washes are extracted with ether to remove a small quantity of dissolved glycol, and the residue obtained after evaporation of the ether is combined with the main portion of glycol. The crude glycol is broken up into small

pieces and air-dried, yielding about 55 g. (95% yield) of fairly pure 1,2-tetradecanediol, m.p. about 65°, iodine number about 4. This is recrystallized from methanol (8 ml./g.) at 0°, yielding about 40 g. of pure product, m.p. 68-68.5°.

1,2-Cyclohexanediol.[204] To a mixture of 105 g. of 98-100% formic acid and 13 g. (0.115 mole) of 30% hydrogen peroxide, 8.0 g. (0.097 mole) of cyclohexene is added. The immiscible layers are shaken together briefly; spontaneous heating occurs and the suspension becomes homogeneous at 65-70° where it is held for two hours on the steam bath. Most of the formic acid is removed by distillation, and the residue is heated on the steam bath for forty-five minutes with 50 ml. of 20% sodium hydroxide. After cooling, the yellow solution is neutralized with hydrochloric acid and evaporated to dryness under vacuum. The resulting solid is distilled, yielding 10.25 g. of a fraction, b.p. 128-132°/15 mm., which solidifies immediately. Recrystallization from acetone gives 7.9 g. (70% yield) of trans-1,2-cyclohexanediol, m.p. 102-103°.

HYDROXYLATION WITH HYDROGEN PEROXIDE-ACETIC ACID

9,10-Dihydroxystearic Acid, High Melting Isomer.[505] A well-stirred solution consisting of 270 g. (0.898 mole) of elaidic acid (containing 94% elaidic acid and 6% saturated acids), 810 ml. of glacial acetic acid and 20 g. of concentrated sulfuric acid is heated to 40°, and 123 g. of 25.5% hydrogen peroxide (0.925 mole) is added dropwise over a period of fifteen minutes. The reaction is only slightly exothermic. A granular precipitate begins to form after about thirty minutes, and increases in bulk as the oxidation proceeds. The total reaction time at 40° is five hours. The reaction mixture is then poured into several volumes of hot water (95-100°) and stirred well for several minutes. The mixture is cooled to room temperature and filtered, and the precipitate is washed well with cold water. The product, which weighs about 300 g. and consists of a mixture of 9,10-dihydroxystearic acid and hydroxyacetoxystearic acids, is heated at 100° for one hour with an excess of 2N sodium hydroxide, and then poured into excess hydrochloric acid,

with stirring. The granular precipitate is filtered and washed acid free. It weighs about 280 g. and consists of somewhat impure 9,10-dihydroxystearic acid, m.p. 125-128°. Crystallization from 95% ethyl alcohol (7 ml./g.) at 0-5° yields 220 g. of pure 9, 10-dihydroxystearic acid as glistening plates, m.p. 130-131°. The yield is 78%.

HYDROXYLATION WITH PERFORMIC ACID

2,3-Dihydroxynonanoic Acid.[204] Twenty grams (0.13 mole) of 2-nonenoic acid is slowly added to a well-stirred solution of performic acid prepared by the reaction of 69 g. of 98-100% formic acid, 19 g. (0.5 mole) of 90% hydrogen peroxide and 0.50 g. of concentrated sulfuric acid. The emulsified mixture is heated to 55-60° to start the reaction, and is then held at this temperature for two hours while being stirred continuously. ~~with continuous stirring.~~ The temperature is then allowed to rise to 95° until the spontaneous reaction is over (twenty-five minutes) and the excess peracid largely destroyed. Most of the formic acid is removed by vacuum distillation, and the residue is saponified on the steam bath for one-half hour with 175 ml. of 10% sodium hydroxide. After acidification with hydrochloric acid, the oily product is extracted with ether, and the extract is dried over anhydrous sodium sulfate. Evaporation of the ether yields a waxy solid, which is suspended in benzene and filtered, yielding 2,3-dihydroxynonanoic acid as white slippery flakes. Concentration of the filtrate followed by addition of ligroin, gives two additional crops, the total yield of product being 12.4 g. (51%). On crystallization from ethyl acetate or water, 2,3-dihydroxynonanoic acid, m.p. 118-118.5°, is obtained.

TABLE I

UNSATURATED SUBSTANCES CONVERTED TO OXIRANE (α-EPOXY) COMPOUNDS BY EPOXIDATION WITH PERBENZOIC ACID

Unsaturated Substance	Yield of Oxirane Compound %	Reference
3(β)-Acetoxy-20-oxo-5-allo-Δ^{16}-pregnene	55	414
Acetyllinalool	-	431
20-Allopregnene-(3β,17β)-diol-3-monoacetate	-	476b
20-Allopregnene-(3β,17β)-dioldiacetate	Quant.	476b
Allyl alcohol	-	425,430
d-α-Amyrilene	-	473
β-Amyrilene	-	473,474
β-Amyrin	-	473,474
5-Androstene-3,17-dione	30	465
9-Androstene-3,17-dione	-	412
9-Androstene-3(β)-ol-17-one acetate	-	453
β-Anhydrodigoxigenin diacetate	75	416
β-Anhydrodihydrodigoxigenin diacetate	65	416
Anhydro-[4-(enol)-acetobutyl alcohol]	47	49,51
1-Anisyl-2,2-diphenylethylene	90	311,556
1-Anisyl-1-(m-methoxyphenyl) ethylene	80	321
1-Anisyl-1-(o-methoxyphenyl) ethylene	-	321
Apocholenic acid	-	566
Apocholic acid	-	126,162,567
Benzaldehydephenylhydrazone	60	54
1-Benzyl-1-cyclohexene	-	369
1-Benzyl-2,2-diphenylethylene	85	311

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Benzylethylene	60 - 80	323,325
Benzylideneacetone	-	431
1-(2-Biphenylyl)-1-phenyl-2,2-diethylethylene	75	133
Brassidic acid	55	196
p-Bromobenzylethylene	-	439
1-Bromo-2-methoxy-4-pentene	85	395a, 401a
4-(p-Bromophenyl)-1-butene	75	439
Butadiene	42	438
1-Butyl-1-cyclohexene	-	369
1-Butyl-2,2-diphenylethylene	85	311
1-Isobutyl-2,2-diphenylethylene	95	311
$C_{15}H_{24}$(Two C = C)	-	313
Camphene	-	208
Caprylene	-	425,428
d-$\overset{3}{\triangle}$-Carene	70	22
Carotene	10 - 15	207
Caryophyllene	70-Quant.	476,536
1-Chloro-1-cyclohexene	-	369,373,373a
1-Chloro-2-cyclohexene	-	371,373
1-Chloro-1-cyclopentene	-	373
1-Chloro-2-cyclopentene	-	373
1-Chloro-1-heptene	31	426
2-Chloro-1-methyl-1-cyclohexene	-	373
3-Chloro-1-methyl-3-cyclohexene	-	371,373

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
2-Chloro-1-methylenecyclohexane	-	374
1-Chloromethyl-2-phenylethylene	-	220
2-Chloro-2-octene	25	426
4-Cholestene	-	247,413
5-Cholestene	-	413,467
Δ^{5}-Cholestene-3-one	58	465
γ-Cholestenyl acetate	-	159a,412b
Δ^{7}-Cholesteryl Acetate	12	412b
Cholesterol	75	413,465,559
Cholesteryl acetate	75	465
Cholesteryl benzoate	84	261,493
Cholesteryl chloride	50	247
Cinnamyl acetate	70	273
Cinnamyl alcohol	78	273
Citral	-	425,431
Citronellal	-	425,430
Citronellol	-	308a
Copaene	Quant.	139a
Crotonic acid	20	136
Crotyl alcohol	11	273
1-Cyano-2-cyclohexene	-	374a
1-Cyano-2-cyclopentene	-	374a
Cycloheptene	Quant.	94
1,3-Cyclohexadiene	85-90	43

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Cyclohexene	Quant.	85,308
Cyclopentene	-	85
1-Decene	Quant.	464
Decene	-	425
Dehydroandrosterone	60	538,539
3-Trans-dehydroandrosterone	-	351
Trans-dehydroandrosterone acetate	50	469
Dehydroergosteryl acetate-maleic anhydride adduct	-	261
Dehydroisoandrosterone	Fair	201
Dehydroisandrosterone acetate	40	200
3,6-Diacetoxy-5-methylnorcholestane	20	405
3(β),21-Diacetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	25	415
3,4-Diacetoxystyrene	-	281a
Diallyl	-	84
1,1-Dibenzyl-2-anisylethylene	-	521
Dibromodehydroergosteryl acetate-maleic anhydride adduct	80	56-1
1,1-Dicyclohexylethylene	76	547
Dicyclopentadiene	70	38,564
1,1-Diethoxy-2-butene	25	220
1,1-Diethyl-2-anisylethylene	-	521
1,1-Diethyl-2-phenylethylene	70 - 90	326
Dihydro-β-amyrilene	-	474
Dihydrocaryophyllene	69	476
Dihydrocyclopentadiene	80 - 90	564

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
1,2-Dihydronaphthalene	-	512
2,3-Dihydronaphthalene	-	93
1,4-Dihydronaphthalene	-	93,512
5,6-Dihydro-1,2-pyran	58	401
3,7-Dihydroxycholenic acid	70	565
4,5-Dihydroxy-2,6-octadiene	-	273
2,3-Dihydroxy-1-propene (acetone compound)	-	218
Diisobutylene	-	425,429
1,1-Dimethyl-2-anisylethylene	-	515,521,522
2,3-Dimethyl-2-butene	-	429
Dimethylcyclohexene	-	429
1,2-Dimethylcyclohexene	75	381
1,3-Dimethyl-1-cyclohexene	-	369
2,4-Dimethyl-1-cyclohexene	-	369
1,1-Dimethyl-2,2-diphenylethylene	-	441
1,2-Dimethyl-1,2-diphenylethylene	-	441
1,1-Dimethyl-2-(m-methoxyphenyl)ethylene	70 - 80	320
1,1-Dimethyl-2-(o-methoxyphenyl) ethylene	70 - 80	320
1,1-Dimethyl-2-methyl-2-phenylethylene	-	334
1,1-Dimethyl-2-phenylethylene	Quant.	326,515,522
1,1-Dimethyl-2-piperonylethylene	60 - 80	516,520
1,1-Dimethyl-2-tolylethylene	60 - 80	516,519
2,4-Dimethyl-4-vinyl-1-cyclohexene	-	313
1,1-Dipropyl-2-anisylethylene	-	521

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
1,1-Di-p-tolylethylene	-	442
1-Dodecene	Quant.	40,464
Elaidic acid	Good	24,38,88,502
3,9-Epoxy-Δ^{11}-cholenic acid	60	340
Ergosteryl acetate-maleic anhydride adduct	-	56-1
Erucic acid	70	38,196
1-Ethoxy-2-cyclohexene	-	370
Ethyl acetoacetate	-	101
1-Ethyl-2-anisylethylene	-	316
1-Ethyl-1-benzyl-2-phenylethylene	70 - 90	326
1-Ethyl-2-(p-bromophenyl) ethylene	75	439
Ethyl cinnamyl ether	-	190
1-Ethyl-2,2-dianisylethylene	-	555
1-Ethyl-2,2-diphenylethylene	-	311,319,555
Ethyl elaidate	-	88
1-Ethyl-1-ethoxy-2,2-dipropylethylene	-	36
Ethyl hendecenoate (undecylenate)	-	327
Ethyl 9,12,15-octadecatrienoate (linolenate)	-	39
Ethyl oleate	-	37,38,39,88
1-Ethyl-2-phenyl-2-anisylethylene	-	555
1-Ethyl-2-phenylethylene	-	316
1-Ethyl-2-propyl-2-anisylethylene	-	554
Ethyl vinyl ether	25	50
Δ^{9}-Etiocholenol-3(α)-one-17	-	194

Table I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
11-Etiocholen-(3α)-ol-(17)-one acetate	>60	311a
Furfuraldiacetate	8	484
Furfuralphenylhydrazone	30	54
Geraniol	-	308a,425,428,431
Glucal	-	52,53
1-Hendecene	Quant.	464
Hendecenoic (undecylenic) acid	25 - 50	237
1-Heptene	-	322
1-Iso-heptene	-	322
3-Heptene	-	209
3-(α)-Hydroxy-$\Delta^{9,11}$-cholenic acid	25	340
3-(α)-Hydroxy-Δ^{11}-cholenic acid	80	341
11-Hydroxy-11,11-diphenyl-1-hendecene	-	327
11-Hydroxy-1-tetradecene	-	327
11-Hydroxy-1-tridecene	-	327
Indene	Quant.	38,85,93,369
α-Ionone	96.5	387
β-Ionone	86	387
Isodihydroxycholenic acid	-	568
Isoprene	30 - 60	438,456
Isosafrole	-	516
Isostilbene	-	295
11-Keto-11-phenyl-1-hendecene	-	327
11-Keto-1-tetradecene	45 - 55	327

TABLE I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
11-Keto-1-tridecene	-	327
Lanostenone	-	44
Lanosteryl acetate	-	44,197
Limonene	60	23,346,425,428
Linalool	-	385,425,431
Linolenic acid	-	37,39
3-p-Menthene	83 - 91	511
1-Menthene-6-ol	-	433
Methyl $\Delta^{14,16}$-3 (β)-acetoxyalloethiocholadienate	-	472a
Methyl 3 (α)-acetoxy-$\Delta^{9,11}$-cholenate	60 - 70	261,484a
Methyl 3 (α)-acetoxy-Δ^{11}-cholenate	50	420
Methyl 3 (β)-acetoxy-Δ^{11}-cholenate	40	420
Methyl 3 (α)-acetoxy-12(α)-hydroxy-Δ^{7}-cholenate	30	56b
1-Methyl-2-anisylethylene	-	316
1-Methyl-1-benzyl-2-phenylethylene	70 - 90	326
Methyl brassidate	-	196
1-Methyl-2-(p-bromophenyl) ethylene	80	439
Methyl Δ^{9}-cholenate	-	454
Methyl Δ^{11}-cholenate	-	4
Methyl cinnamyl ether	85	190,273
3-Methylcyclohexanone (enol acetate)	-	372
1-Methyl-1-cyclohexene	50 - 75	85,308,335,383
4-Methyl-1-cyclohexene	55	369,379
5-Methyl-1-cyclohexene	-	308
6-Methyl-1-cyclohexene	60	308

TABLE I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
5-Methyl-1-cyclohexenyl acetate	-	370a
1-Methyl-1-cyclopentene	-	85,335
d-3-Methyl-1-cyclopentene	-	369
4-Methyl-1-cyclopentene	-	369
Methyl diacetylapocholate	-	368
Methyl 3(α), 12(β)-diacetylapocholate	-	417
Methyl Δ^{14}-3(α), 12(β)-diacetoxycholenate	50	417
Methyl $\Delta^{7,14}$-3(α), 12 (β)-diacetoxycholadienate	-	417
1-Methyl-2, 2-dianisylethylene	-	555
Methyl d-dihydropimarate	-	466
Methyl 3, 7-dihydroxycholenate	-	126
1-Methyl-2, 2-diphenylethylene	-	311,319,555
1-Methyl-1, 2-diphenylethylene	-	517
Methyl elaidate	-	38
Methylenecyclohexane	-	523
2-Methylenedecahydronaphthalene	-	369
Methyl erucate	75	196
1-Methyl-1-ethyl-2-anisylethylene	-	554
1-Methyl-2-ethyl-2-anisylethylene	-	554
4-Methyl-2-ethylcyclohexene	-	369
3-Methyl-1-ethylidenecyclohexane	-	368,369,370a
1-Methyl-1-ethyl-2-phenylethylene	70 - 90	326
Methyl hendecenoate (undecylenate)	-	327
Methyl heptenone	-	430

TABLE I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Methyl 2, 4-hexadienoate (sorbate)	-	248,250
Methyl 3(α)-hydroxy-Δ^{11}-cholenate	45	420
Methyl 3(β)-hydroxy-Δ^{11}-cholenate	55	420
Methyl 3(α)-hydroxy-12-methoxy-$\Delta^{9,11}$-cholenate	95	478
Methyl 3-keto-Δ^{11}-cholenate	70	157
Methyl 3-keto-$\Delta^{4,11}$-choladienate	-	157
Methyl 12-methoxy-$\Delta^{9,11}$-cholenate	-	478
3-Methyl-1-methylenecyclohexane	-	369
3-Methyl-1-methylenecyclopentane	-	369
Methyl 9, 11-octadecadienoate	20	341,486
Methyl 9, 12-octadecadienoate (linoleate)	25 - 40	111,231,411,486
Methyl oleate	67	508
Methyl petroselaidate	-	498
Methyl petroselinate	80	498
1-Methyl-1-phenylethylene	80	46a,180
1-Methyl-2-phenylethylene	-	46a,316,519
Methyl d-pimarate	-	466
4-Methyl-2-propyl-1-cyclohexene	-	369
1-Methyl-1-propyl-2-phenylethylene	70 - 90	326
Methyl ricinelaidate	85 - 95	111,486
Methyl ricinoleate	80	486
Methyl styryl carbinol	-	375
1-Nonene	Quant.	464
9-Octadecene	-	88

TABLE I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Octenes	15	407
Oleic acid	60 - 80	37,38,39,88,408, 447,502,508
Oleyl alcohol	74 - 85	504,508
1-Phenyl-2-anisylethylene	-	515,518
1-Phenyl-2-benzylethylene	-	316
cis-Phenylbutadiene	-	376
4-Phenyl-1-butene	60 - 80	323,325
1-Phenyl-1-cyclohexene	Quant.	85,324,335,382
1-Phenyl-1-cyclopentene	-	85,335
1-Phenyl-2, 2-dibenzylethylene	-	515,518
6-Phenyl-1-hexene	60 - 80	323,325
1-Phenyl-1-(m-methoxyphenyl) ethylene	-	321
1-Phenyl-1-(o-methoxyphenyl) ethylene	-	321
1-Phenyl-4-methylcyclohexene	-	324
5-Phenyl-1-pentene	60 - 80	323,325
1-Phenyl-2-piperonylethylene	-	516,520
1-Phenyl-2-(p-tolyl) ethylene	-	516,519,556
Pinene	-	208,384,425,428,432
5-Pregnene-20-one-3(β), 21-diol-21-monoacetate	70	200
2-Propenyldioxolane	45	220
1-n-Propyl-2-anisylethylene	-	316
1-n-Propyl-1-benzyl-2-phenylethylene	70 - 90	326
1-iso-Propyl-1-benzyl-2-phenylethylene	70 - 90	326
1-n-Propyl-1-cyclohexene	-	369

TABLE I (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
1-iso-Propyl-1-cyclohexene	-	369
1-n-Propyl-1-cyclopentene	-	369
1-iso-Propyl-1-cyclopentene	-	369
1-n-Propyl-2, 2-diphenylethylene	-	311
1-iso-Propyl-2, 2-diphenylethylene	-	311
1-n-Propyl-2-phenylethylene	-	316
1-iso-Propyl-2-phenylethylene	-	316
Pulegone	59	427
Rubber	-	435,436
Squalene	-	447
Stilbene	60 - Quant.	95,295,447,515
Styrene	69 - 75	46a,93,258,259, 281a,447
1,2,3,4-Tetrahydronaphthalene	-	308
Tetraphenylethylene	Quant.	318
Thiopyrine	-	306
1-Tridecene	Quant.	464
1,2,5-Trimethyl-5-isopropenyl-1-cyclohexene	-	313
2,4,4-Trimethyl-1-pentene	40	159a
2,4,4-Trimethyl-2-pentene	70	159b
2,4,4-Trimethyl-1-pentene-3-ol	-	159b
Triphenylethylene	70	311,556

TABLE II

UNSATURATED SUBSTANCES CONVERTED TO OXIRANE (α-EPOXY) COMPOUNDS BY EPOXIDATION WITH MONOPERPHTHALIC ACID

Unsaturated Substance	Yield of Oxirane Compound %	Reference
3(β)-Acetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	45	414
20-Allopregnene-3(β), 17(β)-diol	-	294a,484a
1-(2-Biphenylyl)-1-phenyl-2, 2-dimethylethylene	99	133
Capsanthin diacetate	-	287
α-Carotene	-	285
β-Carotene	Good	284
Cholesterol	60	167
Cholesteryl acetate	73	167,413
Cholesteryl benzoate	50 - 88	41,167
Cryptoxanthin diacetate	-	288
trans-Dehydroandrosterone acetate	25 - 60	469,471
trans-Dehydroandrosterone benzoate	80	469
3(β), 21-Diacetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	70	415
α-Elemolic acid	-	472b
α-Ionone	-	292
β-Ionone	60 - 70	292
Linalool	80	385
2-Lupene	70	274a
Methyl Δ^{14}-3(β)-Acetoxyalloetiocholenate	80	416
Methyl $\Delta^{14,16}$-3(β)-Acetoxyetiocholadienate	Quant.	472
Methyl Δ^{14}-3(β)-Acetoxy-17-isoalloetiocholenate	80	416

TABLE II (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Methyl α-elemolate	-	472b
Methyl α-ionone	60	387
Methyl d-pimarate	-	475
1-Phenyl-2-cyclohexylethylene	-	514
$\Delta^{14,17}$-Pregnadiene-3-one	-	468
Rubixanthin	-	290
17-Vinyl-3,17-isoandrostanediol	65	294a,484b
Vitamin A	-	286,289
Xanthophyll diacetate	6	283
Zeaxanthin diacetate	-	283

TABLE III

UNSATURATED SUBSTANCES CONVERTED TO OXIRANE (α-EPOXY) COMPOUNDS BY EPOXIDATION WITH PERACETIC ACID

Unsaturated Substance	Yield of Oxirane Compound %	Reference
β-Amyrin acetate	-	492
Anethole	62	23
d-Δ^3-Carene	69	22
Castor oil	73	217
Corn oil	71	217
Cottonseed oil	71	217
Cyclohexene	60 - 67	23,104
1-Decene	56	506
1-Dodecene	52	506
3,6-Diacetoxy-5-methylnorcholestane	30	405
Dihydrocaryophyllene	25	386
Elaidic acid	71	217,297,502
Ergosterol-maleic anhydride adduct	-	261
1-Hexadecene	50	506
Isoeugenol	-	23
Isostilbene	-	104
Lard oil	74	217
l-Limonene	63	23
Linseed oil	66	217
Menhaden oil	57	217
3-p-Menthene	59 - 80	511
Methyl elaidate	-	297
Methyl hendecenoate (undecylenate)	40	217

TABLE III (continued)

Unsaturated Substance	Yield of Oxirane Compound %	Reference
Methyl linoleate	-	111,486,503
5-Methylnorcholestane-3,6-dione	55	405
Methyl oleate	45	217
Methyl ricinoleate	-	217
Neatsfoot oil	77	217
1-Octadecene	<40	506
7-Octadecenoic acid (trans)	-	410
1-Octene	35	506
Octenes	28	407
Oleic acid	82	217,502
Oleyl alcohol	80	217
Olive oil	81	217
Peanut oil	75	217
α-Pinene	89	22
Perilla oil	64	217
Rapeseed oil	71	217
Soybean oil	67	217
Stilbene	83 - Quant.	104,511
1-Tetradecene	42	506
Tobaccoseed oil	73	217
2,4,4-Trimethyl-1-pentenes	-	159b, 159c
Triolein	86	217

TABLE IV

UNSATURATED SUBSTANCES CONVERTED TO α-GLYCOLS
BY OXIDATION WITH PERACETIC ACID

Unsaturated Substance	Yield of α-Glycol %	Reference
Allostilbene	-	95
Allylacetic acid	-	103
Allylbenzene	Quant.	96
Allylmalonic acids	-	103
Anethole	55 - Quant.	23,96
Benzyl-2-propenyl sulfone	-	544
Brassidic acid	-	196
16-Bromo-9-hexadecene-1-carboxylic acid	-	267b
Butadiene sulfone	-	544
2-Butene	54	90
d-Δ^1-Carene	-	412
d-Δ^3-Carene	-	22
Castor oil	36	267c /294,480,481,482
Cholesterol	-	412a
Cholesteryl acetate	>50	406
Cocoa butter	-	264
Coconut oil	-	267d
Cyclohexene	Quant.	23,85,96,483
3-trans-Dehydroandrosterone	-	351
3-trans-Dehydroandrosterone tetraacetylglucoside	-	351
Dehydroisoandrosterone acetate	25 - 30	199
9,10-Diacetoxy-12-octadecenoic acid (cis- and trans-)	-	340a
12,13-Dibromooctadecenoic acid	-	340a

TABLE IV (continued)

Unsaturated Substance	Yield of α-Glycol %	Reference
Diisobutylene	-	160,260,269
Dimethylbutadiene sulfone	-	544
iso-Dodecene	-	269
11,12-Eicosenoic acid	-	267
Elaidic acid	75 - Quant.	24,196,262,297,394, 486,502,505,508b
Eleostearic acid	-	99
Eleostearic acid dibromide	-	99
Eleostearic acid tetrabromide	-	99
Erucic acid	58	196,463
Ethyl elaidate	-	486
Ethyl eleostearate	-	99
Ethyl oleate	-	479,481,482,486
Eugenol	Quant.	96
Hendecenoic (undecylenic) acid	95	103,463
Hendecenoic acid dimers	-	463
1-Heptene	-	86
3-Heptene	-	86
1-Hexadecene	-	120,235
Indene	Quant.	96
Isoprene	-	86
β-Isoprene sulfone	60	544
Isosafrole	Quant.	96
Limonene	-	509
Linoleic acid	Small	231,489

TABLE IV (continued)

Unsaturated Substance	Yield of α-Glycol %	Reference
3-Menthene	-	483
Methyl brassidate	Good	196
1-Methyl-1-cyclohexene	-	483
3-Methyl-1,2-butadiene (dimethylallene)	-	86
Methyl elaidate	-	262,265
Methyl erucate	-	196
2-Methyl-1-heptene	-	86
Methyl linoleate	<20	231
Methyl oleate	50	262,265,297
Methyl palmitoleate	-	262
Methyl petroselinate	-	263
iso-Nonene	-	269
Norbornylene	-	70a
9,11,13-Octadecatrienol (eleostearyl alcohol)	-	491
α-9-Octadecene-1,18-dicarboxylic acid	74	267b
Oleic acid	60 - 95	46,196,232,262, 297,394,479,481, 482,486,502,505, 508b,574a
Oleyl alcohol	60	479,481,482,491, 574a
Olive oil	-	267c
Phenylbenzylethylene	Quant.	96
Pregnenonol acetate	25	199
Ricinelaidic acid	-	294
Ricinoleic acid	-	294
Ricinoleyl alcohol	-	491

TABLE IV (continued)

Unsaturated Substance	Yield of α-Glycol %	Reference
Safrole	-	96
Sorbic acid	-	103
Soybean oil	-	270,271,272,395
Stilbene	-	95
Tallow	-	264
2,4,4-Trimethyl-1-pentenes	-	159b, 159c

TABLE V

UNSATURATED SUBSTANCES CONVERTED TO α-GLYCOLS BY OXIDATION WITH PERFORMIC ACID

Unsaturated Substance	Yield of α-Glycol %	Reference
Cinnamic acid	-	204
Cyclohexene	70	204
1-Decene	45 - 75	506
Dimethyl traumatate	-	204
1-Dodecene	40 - 75	506
Elaidic Acid	80 - Quant.	502,505
2-Hendecenoic acid	46	204
10-Hendecenoic (undecylenic) acid	44 - Quant.	232,505
1-Hexadecene	58 - 85	506
Methyl 2-nonenoate	50	204
Methyl ricinoleate	Quant.	505
Monounsaturated acids from human hair fat	-	557
2-Nonenoic acid	25 - 51	204
1-Octadecene	50 - 75	506
1-Octene	58 - 70	506
Oleic acid	60 - Quant.	232, 417a 502, 505
Oleyl alcohol	50 - Quant.	505
Soybean oil	-	271
1-Tetradecene	69 - 95	506
2,4,4-Trimethyl-1-pentene	-	159a
2,4,4-Trimethyl-2-pentene	40	159b

TABLE VI

UNSATURATED SUBSTANCES CONVERTED TO α-GLYCOLS
BY OXIDATION WITH PERBENZOIC ACID

Unsaturated Substance	Yield of α-Glycol %	Reference
Anethole	-	484-1
Anhydroacetobutyl alcohol	-	49
Apocholic acid	-	162,417,567
Aromadendrene	-	536a
Caryophyllene	-	536a
Cedrene	-	536a
Cellobial	90	53
2,4-Cholestadiene	35	56
Crotonic acid	63 - 64	135
Cyclohexene	30	536a
Dihydroergosteryl acetate	-	574
1,1-Diphenylethylene	13	390
Elaidic acid	-	394
Ergosterol	20	574
α-Ergostenyl acetate	-	574
Furan	-	117
Galactal	-	315
Glucal	-	52,510
2-Hexenoic acid	46	137
Isocrotonic acid	62 - 63	135
Lactal	-	48
Linoleic acid	-	409
Methyl dihydroxycholenate	-	162

TABLE VI (continued)

Unsaturated Substance	Yield of α-Glycol %	Reference
3-Methylglucal	30	314
Oleic acid	-	394
2-Pentenoic acid	75	137
cis-Phenylbutadiene	-	376
Rhamnal	75	52,53
Ricinelaidic acid	-	38
Ricinoleic acid	-	38
Sabinene	-	536a
1,2,3,4-Tetracetyl-1,2-glucosene	30	494
Triacetylgalactal	33	315
Triacetylglucal	30	314,510

TABLE VII

SPECIFIC REACTION RATES (k) FOR THE REACTION OF ALIPHATIC AND ALICYCLIC OLEFINS WITH PERACETIC ACID IN ACETIC ACID SOLUTION

Olefin	t°C	k x 10^3 [a]	Reference
Ethylene	25.8	0.19	114,115,499
Propylene	25.8	4.2	114,115,499
1-Pentene	25.8	4.3	114,115,499
1-Pentene	40.9	17.7	115
1-Hexene	25.8-26.2	4.9-5.1	114
1,5-Hexadiene	25.8	8.0	115
1-Heptene	25.8	5.5	115
1-Octene	25	5.0	506
1-Decene	25	4.7	506
Methyl Hendecenoate	25	4.1	217
2-Methyl-1-propene	25.8	92	114,115,499
2-Methyl-1-propene	39.9	300	115
2-Butene	25.8	93	115,499
2-Pentene	25.8	93-5	114,115,499
2-Pentene	40.0	309	115
2-Hexene	25.8-26.2	99-102	114,115,500
2-Hexene	41.0	342	115
3-Hexene	25.8-26.2	129-134	114,115,500
3-Hexene	41.0	457	115
3-Heptene	25.8	110	98
4-Nonene	25.8	105	98
Oleic acid	18	36	111,487

TABLE VII (continued)

Olefin	t°C	k x 10^3 [a]	Reference
Elaidic acid	18	23	111,487
Ricinoleic acid	18	26	111,487
Ricinelaidic acid	18	16	111,487
2-Methyl-2-butene	25.8-26.4	980-1240	114,115,499
2-Methyl-2-butene	40.8	3000	115
Cyclobutene	25.8-26.4	20-22	114,115,500
Cyclobutene	40.1	60.4	115
Cyclopentene	25.8	185-195	114,115,499
Cyclopentene	39.6	526	115
Cyclohexene	15.2	49	115
Cyclohexene	25.8	129	98,114,115,499
Cyclohexene	39.6	404	115
Cycloheptene	25.8	175	98
Cycloheptene	39.8	610	98
1-Methylcyclopentene	25.8	2220	114,115,499
1-Methylcyclopentene	40.9	6660	115

a/ Time in minutes; concentration in moles per liter

TABLE VIII

SPECIFIC REACTION RATES (k) FOR THE REACTION OF ALIPHATIC AND ALICYCLIC OLEFINS WITH PERBENZOIC ACID

Olefin	t°C	$k \times 10^{3}$ [a]	Reference
Sorbic acid (and alkyl sorbates)	0	0.03-0.05	249
Sorbic acid (and alkyl sorbates	20	0.2	249
Sorbamide	0	0.07	249
Sorbamide	20	0.45	249
Crotonaldehyde	20	0.76	75
Sorbyl chloride	0	0.23	249
Sorbyl chloride	20	1.52	249
Hendecenoic (undecylenic) acid	0	16	302
$\Delta^{8,9}$-Menthene-1,2-diol	0	34.7	346
Camphene	0	93.1	346
Oleic acid	0	384	302
Pinene	0	1081	346

a/ Time in minutes; concentration in moles per liter.

TABLE IX

SPECIFIC REACTION RATES (k) FOR THE REACTION OF OLEFINS CONTAINING AROMATIC GROUPS WITH PERACETIC ACID IN ACETIC ACID SOLUTION AND WITH PERBENZOIC ACID IN CHLOROFORM OR CARBON TETRACHLORIDE SOLUTION

	Peracetic Acid			Perbenzoic Acid		
Olefin	t°C	k x 10^{3} [a]	Reference	t°C	k x 10^{3} [a]	Reference
Allylbenzene	25.8-26.1	1.9-2.0	114,115,499	25-30	6-15	89
Allylbenzene	39.6	7.4	115			
Stilbene	25.8-26.3	5.1-6.7	114,115,499	0-1	1-2	89
Stilbene	39.6	16.7	115	15-16	4	89
Stilbene				25-30	18	89
Isostilbene	25.8	11.1	115,499	0-1	2	89
Isostilbene				15-16	9	89
Styrene	25.8	11.3	114,115,499	0-1	2-3.6	89
Styrene	40.8	34.4	115	15-16	8-25	89
Styrene				25-30	35	89
1-Phenyl-1-propene	25.8	46	114,115,499	0-1	3-15	89
1-Phenyl-1-propene	40.8	166	115	15-16	23-54	89
1-Phenyl-1-propene				25-30	110-190	89
Indene	25.8	47	114,115,499			
Indene	41.0	166	115			
1,1-Diphenylethylene	25.8	48	114,115,499			
1,1-Diphenylethylene	39.8	163	115			
1,4-Dihydronaphthalene	25.8	37	114,115,499			
1,4-Dihydronaphthalene	40.9	162	115			
1,2-Dihydronaphthalene	16.3	116	115			
1,2-Dihydronaphthalene	25.8	230-240	114,115,499			
1,2-Dihydronaphthalene	40.9	657	115			

TABLE IX (continued)

Olefin	Peracetic Acid t°C	Peracetic Acid k x 10^3 [a]	Peracetic Acid Reference	Perbenzoic Acid t°C	Perbenzoic Acid k x 10^3 [a]	Perbenzoic Acid Reference
Triphenylethylene	25.8-26.1	5.76	114,115			
Triphenylethylene	41.2	19.5	115			
Methylindene	26.1	599	115			
Methylcinnamylidene acetate				0	0.01	249
1-Phenyl-2-acetylethylene				20	2.5	75
Cinnamic acid (and alkyl cinnamates)				20	0.13	75
Cinnamaldehyde				20	4.7	75
Cinnamyl alcohol				20	202.5	75
1-Phenyl-3-butene				15-16	8-9	89
1-Phenyl-2-butene				15-16	10	89
1 henyl-1-butene				15-16	80	89
Eugenol				0	2.2	346
Isoeugenol				0	127	346
Safrole				0	1.3	346
Isosafrole				0	148	346
1,1-Diphenyl-1-propene				0	17.7	346

a/ Time in minutes; concentration in moles per liter.

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